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## AFOSR - Final Technical Report

### SURFACE TRIBOCHEMISTRY : PFPAE LUBRICANTS

Grant No. AFOSR-F49620-96-1-0253  
Duration - Sept. 1, 1996 to Aug. 31, 1999

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#### **Summary**

The principle objective of this research project was to develop and apply methods for study of the surface chemistry of long chain oligomeric species such as perfluoropolyalkylether (PFPE) lubricants. The PFPEs are liquid lubricants used for a number of very high temperature applications. They typically have molecular weights in the range 1,000 – 10,000 amu and have very low vapor pressures. These molecular weights correspond to structures with ~20 to 200 CF<sub>2</sub> units. The primary accomplishment of the work performed under this grant was the design, development, and testing of a dosing system that allows the introduction of such compounds into an ultra-high vacuum system used for surface analysis. This device has been tested with a study of the adsorption and desorption of long chain alkanes and PFPEs on the surface of graphite. The device is now being used for studies of the adsorption and desorption of high molecular weight, low vapor pressure species such as PFPE liquid lubricants and vapor phase lubricants such as tricresylphosphate (TCP).

## 1. OBJECTIVE

Tribology is of critical importance to a number of Air Force technologies and lubricant surface chemistry is a critical component of tribology. Much of the research in the P.I.'s laboratory is focused on the study of the surface chemistry of lubricants and on understanding the fundamentals of friction and lubrication. Typically the needs of the Air Force are for lubricants that operate at much higher temperatures than those of traditional applications. At the time of the writing of the proposal the use of perfluorinated fluids such as Krytox and Fomblin were being considered for a number of applications. These are perfluoropolyalkylethers (PFPEs) with molecular weights in the range 1,000 – 10,000 amu having ~20 to 200 carbon atoms. These oligomers are extremely thermally stable fluids to very high temperatures and have very low vapor pressures. Although they are no longer considered to be of direct importance for Air Force applications they are of critical importance in the magnetic data storage industry and thus of important although indirect interest. A second method for high temperature lubrication is through the use of vapor phase lubricants such as tricresylphosphate (TCP),  $(\text{CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}=\text{O}$ . This is also a high molecular weight compound (368 amu) with a relatively low vapor pressure. TCP functions as a lubricant by being exposed to the surface through the vapor phase and reacting to produce thin lubricating films of polyphosphate glass containing carbon. One of the primary objectives of the research in the P.I.'s laboratory over the past decade has been to understand the details of the chemical mechanism by which such lubricant compounds either interact with or react with surfaces.

Prior to the funding and completion of the project described in this report our use of surface science methods to study lubricant surface chemistry was limited to the use of small compounds which model the surface chemistry of real lubricants. This is primarily due to experimental limitations since many of the methods used to study the reactions of molecules on surfaces are limited to use under ultra-high vacuum conditions. Such vacuum environments allow surfaces of metals to be cleaned and maintained for periods that are long enough for molecules to be adsorbed and then analyzed using surface sensitive spectroscopic tools. Many such tools are based on the use of electron or ion based techniques that also require a vacuum environment. The primary limitation that this has traditionally placed on the compounds used in such studies is that they be gases at room temperature or at least liquids with relatively high vapor pressures. Such compounds are readily introduced into vacuum chambers through leak valves for

adsorption on surfaces. This obviously places a severe constraint on the study of lubricant surface chemistry where the lubricants are low vapor pressure compounds such as the PFPEs or TCP.

The goal of the proposed project was to develop instrumentation for the adsorption of high molecular weight, low vapor pressure species onto surfaces in ultra-high vacuum. This instrumentation was then to be used for the study of the adsorption of PFPE lubricants on surfaces. A high molecular weight doser that is useful for such an application must meet a number of specifications. It must allow introduction of the adsorbate into the vacuum system and adsorption on the surface of interest without contaminating the rest of the chamber. Secondly it must be possible to analyze the vapor emanating from the doser in order to ascertain the identity and purity of the material being adsorbed on the surface of interest. Only at this point is it possible to begin to study the surface chemistry of such species.

This report describes the successful development of a high molecular weight doser for use under UHV conditions. This system meets the criteria described above and is now in use for a number of studies of lubricant surface chemistry.

## **2. TECHNICAL PROGRESS**

### **2.1 High Molecular Weight Doser**

The bulk of the effort expended on this project was on the development, testing, and debugging of the high molecular weight doser. This doser attached to the UHV chamber is shown in figure 1. The chamber at the left houses the sample surface, leak valves, a quartz crystal microbalance, and a quadrupole mass spectrometer. The sample is mounted on a manipulator that allows it to be moved within the chamber and it can be heated and cooled in the range 100K – 1000K. The dosing tube can be moved into the chamber up to the ionizer of the quadrupole mass spectrometer. In this way the QMS can be used to analyze the material emanating from the end of the doser. Once it has been determined that the vapor from the end of the doser is pure, the tube can be withdrawn from the QMS and the sample can be lowered in front of the doser in order that the effluent adsorb on its surface.

The doser itself is shown in expansion in figure 2. At the left is the glass vial that holds the low vapor pressure liquid or solid. This is heated with a controlled temperature heating jacket to temperatures in the range 300K – 550K. A gate valve between the sample vial and the doser

allows it to be removed without venting the entire doser. The doser consists of a long collimating tube which is mounted on a linear motion translator and can be moved all the way into the chamber or retracted from the chamber completely and isolated with a gate valve. Heating the material in the vial elevates its vapor pressure to the point that it is high enough to create a useful flux emanating from the end of the collimating tube. The collimating tube serves to trap material that does not travel in a direct line of sight trajectory from the hot vapor zone to the surface in the UHV chamber. The doser is fitted with its own ion pressure gauge and with pumping so that samples can be introduced and purified without venting the main UHV chamber.

The protocol for using the high molecular weight doser requires extensive purification of samples. Because it is always the case that high vapor pressure contaminants will evaporate from the samples at lower temperatures than the material of interest, these contaminants must be pumped away before opening the gate valve to the UHV chamber. Even then it is necessary to use the mass spectrometer to analyze the material coming from the end of the collimating tube. With low vapor pressure materials purification can require a great deal of effort before the effluent is purified to the point of being useful. Once the sample is purified the surface in the chamber can be positioned in front of the doser for a predetermined period of time with the doser at a fixed temperature in order to adsorb the high molecular weight species.

## **2.2 Desorption of High Molecular Weight Oligomers from Surfaces**

The primary technical accomplishment of this proposal has been the design, fabrication, and testing of the high molecular weight doser described above. It has required several iterations to the original design in order to reach the stage of having a useful, operational doser. In addition a great deal of effort has been expended to come up with a protocol for using this device such that it is capable of generating a high flux of pure, high molecular weight species in the gas phase. Having achieved this we have now built a second such device in the laboratory for use with vapor phase lubricants.

The initial testing of the high molecular weight doser has been performed using a series of straight chain alkanes adsorbed on graphite. This choice was based on the fact that the alkanes can be found in monodispersed form with molecular weights ranging from 16 ( $\text{CH}_4$ ) to 842 ( $\text{C}_{60}\text{H}_{122}$ ) amu and vapor pressures covering many orders of magnitude. As an example figure 3

shows the desorption of  $C_{32}H_{66}$  from the surface of graphite as a function of coverage. This molecule is a solid at room temperature and yet we have been able to introduce it into vacuum and deposit it on the graphite surface with a very high level of control. The high temperature desorption peaks correspond to the desorption of the monolayer from the graphite surface. The area of this feature grows with increasing coverage but the peak desorption temperature does not shift. This indicates a first-order desorption process with a desorption energy that is independent of coverage. The low temperature desorption features are due to the multilayer. This data is part of a comprehensive study that we have performed using the high molecular weight doser to measure the desorption energies of ~20 straight chain alkanes ranging in size from  $C_5H_{12}$  to  $C_{60}H_{122}$  adsorbed on the surface of graphite. This data is quite unique and would not have been possible without the high molecular weight doser.

The original intent of the project was to use the doser to study the surface chemistry of the PFPE lubricants. Although these are no longer considered to be of direct interest to Air Force technologies they are of indirect importance through the fact that they are used to lubricate the surfaces of magnetic storage media such as hard disks. In addition to the study of alkanes we have measured the desorption energies of a particular type of PFPE known as Fomblin Zdol adsorbed on the graphite surface. The data are shown in figure 4 for a sample that has been fractionated to have an average molecular weight of ~1300 amu. As in the case of the alkanes these TPD spectra show a monolayer desorption feature at high temperature and a multilayer desorption feature at low temperature. These are not quite as well defined as those for the alkanes because the Fomblins are not truly monodispersed. Nonetheless they do represent a unique set of data that could not have been obtained without this device.

Current work in the P.I.'s group is focused on the surface chemistry of tricresylphosphate which is the compound used most commonly as a vapor phase lubricant. This is a high molecular weight (368 amu) liquid at room temperature and cannot be introduced into a UHV chamber through a standard leak valve. In order to use this compound a second high molecular weight doser has been assembled for use with that project.

### 3. TRANSITIONS

Our tribological efforts supported by the AFOSR have resulted in transitions of technology and participation in research/development programs several government labs and companies.

*Seagate Magnetics Corp.* We have been supported to study the surface chemistry of fluorocarbon lubricants on the amorphous carbon films used for protection of the surface of magnetic recording media. Contact person is Dr. Jing Gui.

*National Storage Industries Consortium.* We have been supported to study bonding of fluoroether lubricants to amorphous carbon films. Contact person is Dr. Singh Bhatia.

*Platinum Research Organization.* Studies of lubricant film deposition. Contact is Mr. Cork Jaeger.

*Quinta Corp.* We have studied the decomposition and desorption of long chain Fomblins from the surfaces of amorphous carbon films. Contact person is Dr. Paul Jones.

#### **4. PERSONNEL**

The grant has supported the first two and half years of the Ph.D. program of Mr. Kris Paserba who is due to receive a degree in May of 2001.

#### **5. PUBLICATIONS**

1. K. Paserba, A.J. Gellman, "Chain length dependence of n-alkane desorption energies from the surface of graphite" in preparation
2. K. Paserba, A.J. Gellman, "Conformational isomerism effects on the desorption energetics of n-alkanes from the surface of graphite"

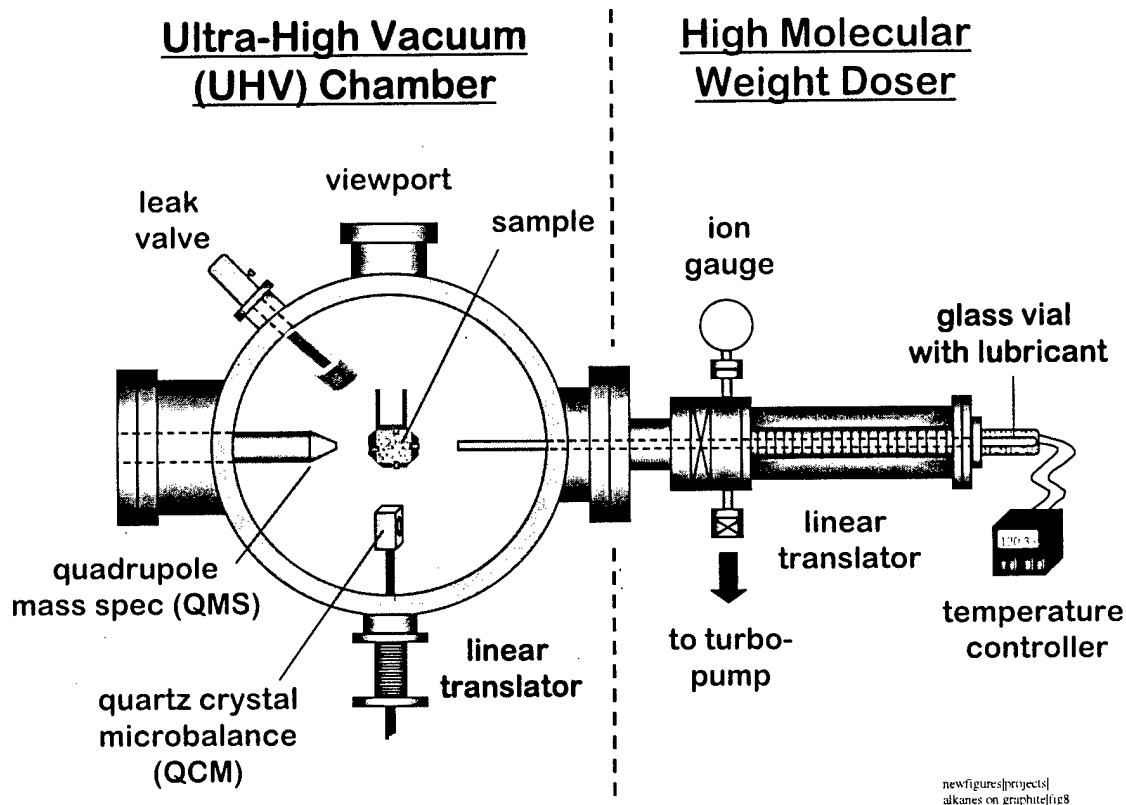


Figure 1. An illustration of the UHV chamber fitted with the high molecular weight doser developed during the course of this project. The chamber is on the left and housed a sample surface for study. In addition it contains a quadrupole mass spectrometer used for analysis of the effluent from the doser, and a quartz crystal microbalance for the measurement of absolute masses of material emanating from the doser.



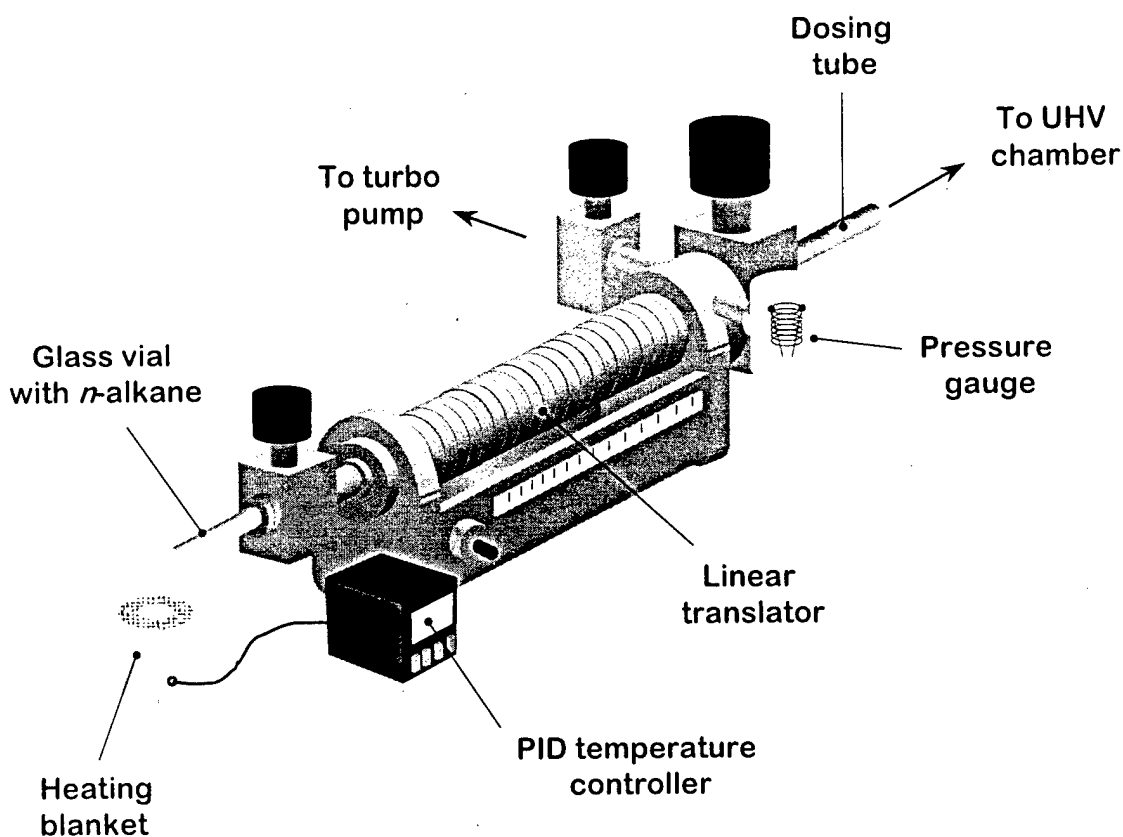


Figure 2. An illustration of the high molecular weight doser. At the left is a glass vial housing the liquid or solid sample to be introduced into the chamber. This can be heated using a controlled temperature heating mantle. The vial is attached through a gate valve to a long collimating tube that serves to direct the vapor directly at the sample surface in the chamber. The entire device is mounted on a linear motion feedthrough that allows it to be extracted from the chamber. In addition it has its own pumping to allow materials to be degassed and purified of high vapor pressure contaminants prior to introduction into the UHV chamber.

# TPD - C<sub>32</sub>H<sub>66</sub> / Graphite

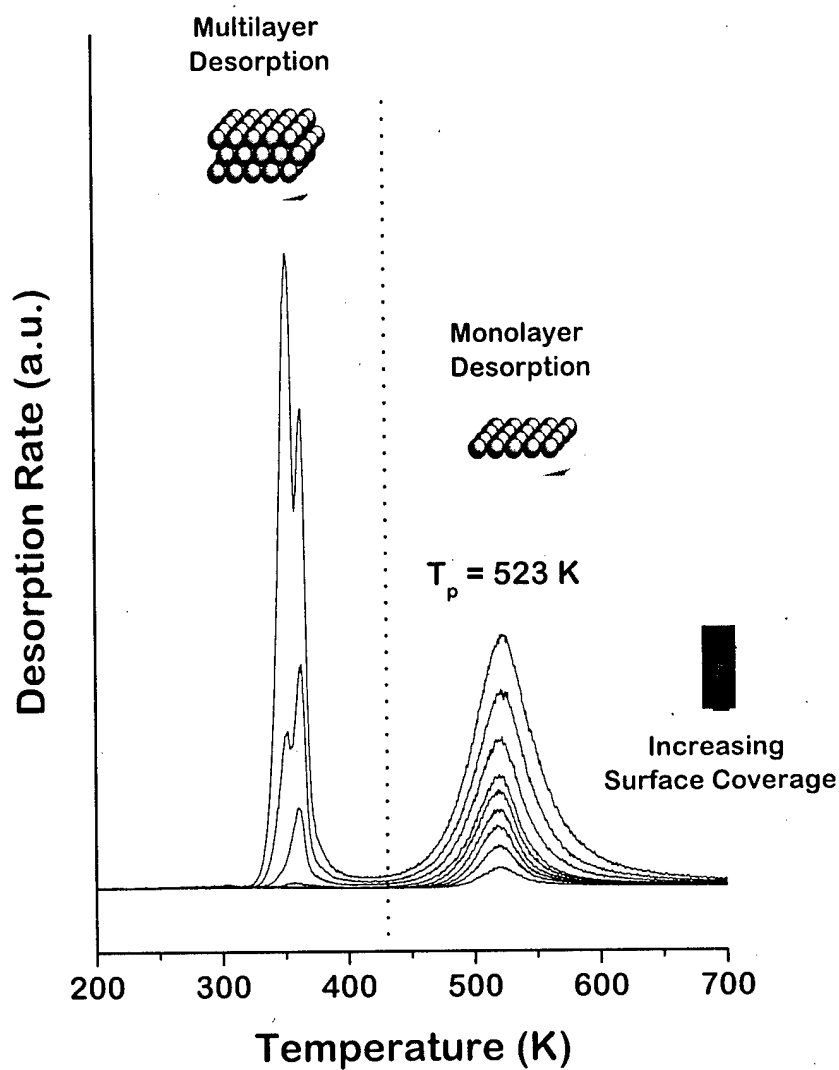
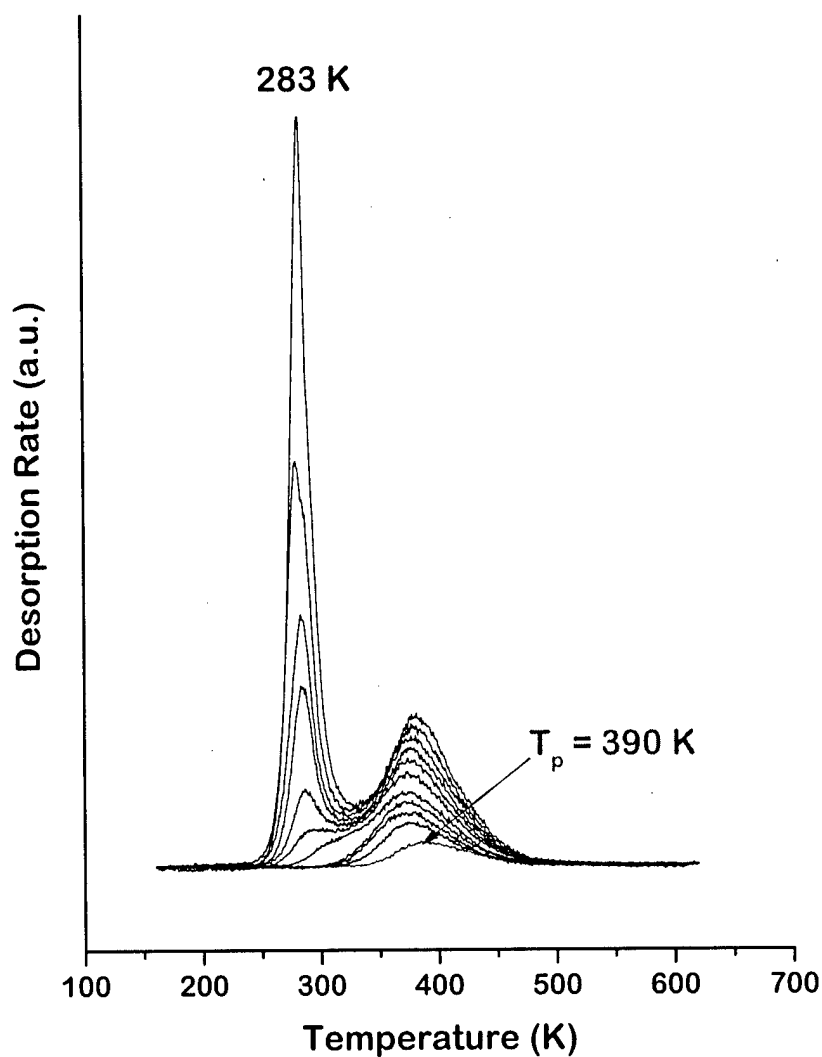


Figure 3. Desorption spectra of C<sub>32</sub>H<sub>66</sub> from the surface of graphite as a function of increasing coverage. The high temperature peak at 523K is due to the desorption of the monolayer bonded directly to the graphite surface. The lower temperature peaks are due to the multilayer.

## TPD - Fomblin ZDOL / Graphite

( $M_n = 1324$  g/mole)



newfigures/projects/  
large mol doserfig21

Figure 4. The desorption of Fomblin Zdol (1324 amu) from the surface of graphite as a function of increasing coverage. Fomblin Zdol is a PFPE lubricant. The desorption feature at 390K is due to the monolayer on the surface while the desorption feature at 283K is due to the multilayer.